

PHASE TRANSFORMATIONS IN A CERAMIC MOLD FILLED WITH HIGH ALLOY

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After a high alloy is poured into a corundum-sillimanite mold the phase composition in the mold changes and the chemical activity of the mold increases. The post-kilning and post-filling phase composition of disthene-sillimanite is studied. It is proposed that alumina be added to disthene-sillimanite and the mixture be kilned at temperature 1643 K. As a result mullite will form and have a positive effect on the quality of the mold. The new refractory powder can be used to form the lining layer of the ceramic mold.

Key words: disthene-sillimanite, ceramic mold, mullite, silica, refractory powder, kilning.

Ceramic molds for obtaining precise castings from high alloys are made from KDSP disthene-sillimanite concentrate and organosilicon binder by casting using smelted models. The advantages of molds based of KDSP are: low linear thermal expansion coefficient $CLTE = 5.1 \times 10^{-6} \text{ K}^{-1}$, high dimensional accuracy — GOST 25347–82 acceptance criterion 8–10, small deformation under load in the temperature interval 1073–1473 K — $(0.25–1.9) \times 10^{-3} \text{ m}$, high casting-surface purity $R_z = 20–40 \text{ }\mu\text{m}$, adequate post-kilning strength — 2.5–4.5 MPa, comparatively high gas permeability 7.0–7.5 and thermal conductivity in the crystallization temperature interval of the alloys $\lambda = 7.3 \text{ W/(m} \cdot \text{K)}$ [1, 2]. These properties of molds determined their predominate use for obtaining especially demanding castings, for example, turbine blades of jet engines. The quality of such castings is checked using x-ray diffraction, luminescence, and other checking methods, and some castings are rejected even by visual examination. For this reason, the improvement of the technology of making ceramic molds and stabilizing their properties during pouring of high alloys are very topical today.

A drawback of ceramic molds with disthene-sillimanite fill is the presence of free silica in the fill. For high-temperature vacuum pouring the free silica possesses high chemical activity and causes contamination of the surface of the casting. This occurs by several mechanisms [3, 4]:

- direct oxidation of the elements of the alloy such as aluminum and titanium with their oxides forming on the casting surface;

- incongruent evaporation of silica with formation of predominately SiO , O_2 , as well as atomic oxygen; and,
- local formation of liquid fayalite on interaction with iron oxide, present in small quantities in disthene-sillimanite.

Free silica can appear in a ceramic mold of this type for two reasons.

1. The transformation of organosilicon binder during kilning of molds results in the appearance of 10–13% crystalline silicon in the composition of the molds. There are several directions for replacing the binder or decreasing its quantity, but for especially demanding castings this question remains unresolved to this day.

2. The possibility of mullitization of KDSP with free silica being released when metal is poured into a ceramic mold. This process has not been adequately studied and requires more detailed analysis.

Disthene (kyanite) and sillimanite with the general chemical formula is $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (the computed composition by weight is 63.1% Al_2O_3 and 36.9% SiO_2) are present in the disthene-sillimanite composition. These substances differ considerably by crystal structure and the optical and other properties. The closest packing of the oxygen atoms is observed in the crystal lattice of disthene and considerably looser packing is seen in the sillimanite lattice. The disthene content is 39–40% in disthene-sillimanite and 56–57% in sillimanite. On heating these materials transform into mullite, cristobalite, and glass in the presence of impurities:



The greatest growth on kilning is observed during mullitization of disthene (16–18%). According to the data obtained by different authors, its decomposition temperature

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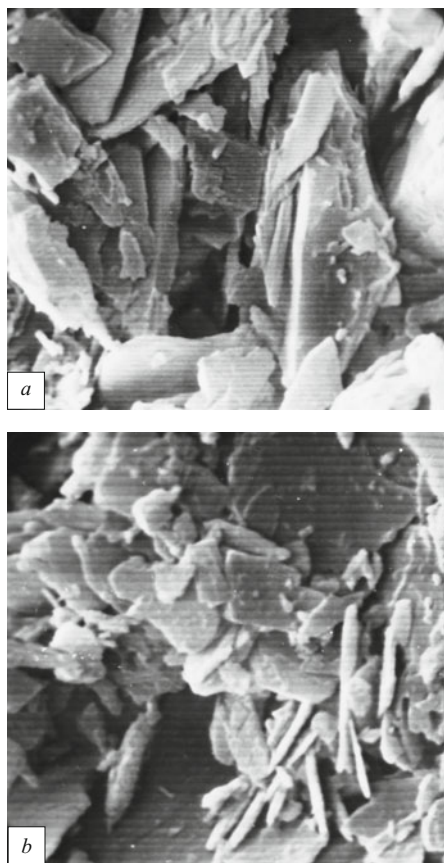


Fig. 1. Disthene-sillimanite powder after drying (*a*) and after kilning (*b*) at temperature 1623 K for 4 h ($\times 3250$).

fluctuates from 1373 to 1653 K. After soaking for 24 h at temperature 1373 K very thin edges, which are mixtures of mullite and a glassy substance appear on the disthene grains. Silica precipitates from disthene at temperatures above 1573 K [5].

Sillimanite differs from disthene by a substantially lower density and on kilning it gives smaller growth (7–8%) during the mullitization process. The onset temperature of sillimanite decomposition is 1673 and 1823 K [6]. When disthene-sillimanite undergoes mullitization up to 12.5% free silica precipitates [7]. The impurities of disthene-sillimanite — Fe_2O_3 , TiO_2 , MgO , and CaO — can have a definite effect on phase transitions; the content of these impurities does not exceed 0.8, 1.5, 0.4, and 0.2%, respectively.

Figure 1 displays images of KDSP powder after drying (*a*) and after kilning (*b*) at 1623 K for 4 h. Their distinguishing feature is the appearance of mullite needles in the kilned powder.

A qualitative x-ray phase analysis of KDSP powder and the liner layer of ceramic molds after the molds are filled in the UPPF-3 and PMP-2 apparatus was performed with a DRON-3M analyzer. In the first apparatus, preheated in a crucible to 1173 K, a ceramic mold is filled with an alloy at temperature 1873 K in vacuum 1.33 Pa; in the second apparatus the mold is heated in a through furnace to temperature

1873 K, and the melting metal fills the cavity of the mold. The vacuum in the pouring zone is 0.65 Pa. The phases were identified according to the data given in [8, 9].

Figure 2*a* and *b* show the x-ray diffraction patterns of the initial KDSP powder and the liner layer of the ceramic mold filled in the UPPF-3 apparatus. It is evident that in the second case mullitization of disthene starts in disthene-sillimanite, which can be judged according to the decrease of the intensities of the interference lines of disthene $d/n = 3.18$, 1.94, and 1.77 Å; sillimanite does not undergo any transformations under these conditions.

The cycle time is longer in PMP-2. As a result conditions are created for complete mullitization of disthene and partial mullitization of sillimanite; new phases appear — mullite and $\alpha\text{-Al}_2\text{O}_3$ (Fig. 2*c*). Mullite is characterized by intensification of the lines $d/n = 3.48$, 2.38, and 2.08 Å. The appearance of $\alpha\text{-Al}_2\text{O}_3$ is due to the oxidation of aluminum, present in the alloy, by oxygen in silica. Thus, in the course of heating molds in PMP-2 the content of free SiO_2 on the surface of the mold increases as a result of mullitization of disthene and can reach 20%, which causes oxidation of the elements of the alloy.

To decrease the chemical activity of KDSP the powder must first be mullitized. For this, the initial KDSP was mixed with GOO technical-grade alumina and kilned at 1593–1643 K in an oxidizing atmosphere; in the process disthene is completely transformed into mullite. The x-ray diffraction pattern in Fig. 2*d* shows that the main phases are mullite and sillimanite; the $\alpha\text{-Al}_2\text{O}_3$ phase is also present and appears as a result of a transition from $\gamma\text{-Al}_2\text{O}_3$, which is the base of alumina at temperatures above 1483 K. The amount of alumina is determined from the stoichiometric ratio of the mullitization reaction. The alumina which has not reacted during preliminary kilning interacts with SiO_2 , which precipitates from the sillimanite as the mold is heated in the pouring apparatus.

It is shown in [10] that mullite synthesis starts at 1173 K and is completed at 1673 K only when the initial mixture is pre-ground in a planetary mill to nanostructures as a result of restructuring of Si–O–Si structures and formation of Si–O–Al bonds in the same layer.

Figure 2*e* displays the x-ray diffraction pattern of mullitized KDSP which has passed through PMP-2. It is evident that the intensity of the $\alpha\text{-Al}_2\text{O}_3$ peaks ($d/n = 3.48$, 2.38, 2.08, and 1.6 Å) and sillimanite peaks ($d/n = 3.38$, 3.77, and 1.37 Å) decreased, while the intensity of the mullite lines ($d/n = 5.35$, 1.84, and 1.44 Å) increased. This indicates mullitization of sillimanite and formation of secondary mullite from $\alpha\text{-Al}_2\text{O}_3$ and precipitated SiO_2 .

Iron oxide is the most thermodynamically unstable compound under the pouring conditions indicated. According to the data of [11], the amount of Fe^{3+} introduced can reach 3%. As a result of the closeness of the ionic radii of Al^{3+} and Fe^{3+} (0.057 and 0.076 nm) partial isomorphic substitution of Fe^{3+} for Al^{3+} occurs in the mullite lattice. The total amount of iron

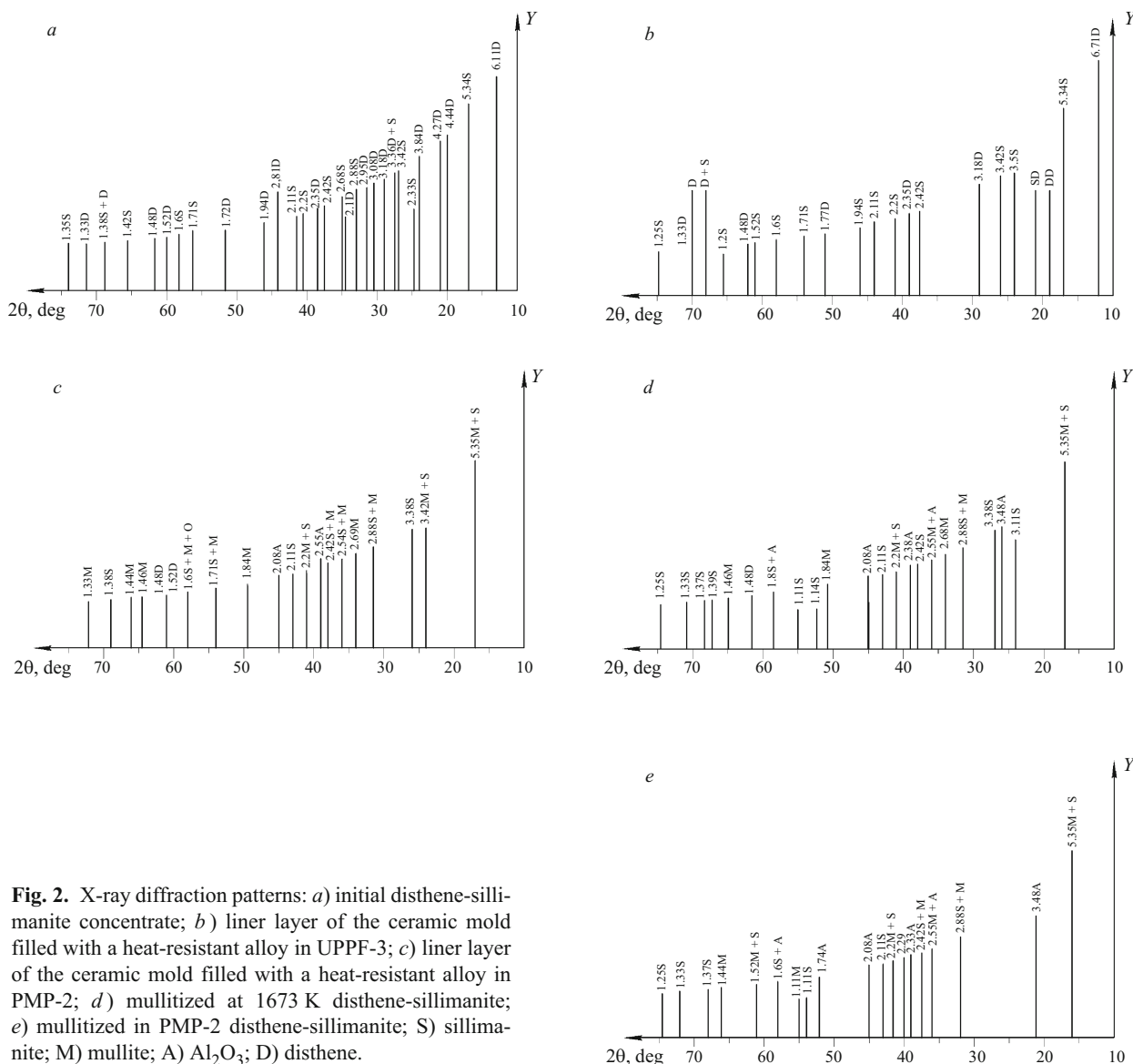


Fig. 2. X-ray diffraction patterns: *a*) initial disthene-sillimanite concentrate; *b*) liner layer of the ceramic mold filled with a heat-resistant alloy in UPPF-3; *c*) liner layer of the ceramic mold filled with a heat-resistant alloy in PMP-2; *d*) mullitized at 1673 K disthene-sillimanite; *e*) mullitized in PMP-2 disthene-sillimanite; S) sillimanite; M) mullite; A) Al_2O_3 ; D) disthene.

in the mullite lattice (interstitial and substituted) depends on the kilning temperature. At 1473 K all iron is in the glass phase. At 1623 K Fe^{3+} partially enters the mullite lattice. At higher temperatures iron partially leaves the lattice.

In summary, the following conclusions can be drawn on the basis of the results obtained in this work.

Additions of alumina to disthene-sillimanite make it possible to bind the silica which has precipitated during mullitization of disthene-sillimanite, which lower the chemical activity of a ceramic mold to the high alloy poured into it. The amount of alumina is determined on the basis of the stoichiometric ratio of the mullitization reaction and the amount of binder.

When the molds are filled in the UPPF-3 apparatus the KDSP powder should be kilned at 1623 K, since prior to filling the mold is heated to 1173 K. The activation energy for the Fe^{3+} ion to leave mullite is evidently much higher than

the activation energy of FeO in fayalite ($2\text{FeO} \cdot \text{SiO}_2$, melting temperature 1478 K), so that the elements of the alloy are less likely to undergo oxidation.

When a mold is filled in the PMP-2 apparatus alumina must be added to the suspension in order for the mullitization process to be completed as the mold passes through the zones of the furnace.

The content of iron oxide in the liner layers of the mold must be low.

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